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THE EFFECT OF BIOAUGMENTATION ON SOIL MICROCOSMS CONTAMINATED WITH MINE TAILINGS

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Abstract

This work is part of a preliminary study on the remediation of soils contaminated by residues derived from mining activities. The effect of bioaugmentation was investigated in microcosm tests in which S-oxidizing microorganisms were supplemented to improve the microbial activity of an indigenous soil microbiota. The results obtained indicate that the variable studied had a dissimilar effect on metal mobilization (Fe, Zn and Pb) from the contaminated soil towards both the aqueous phase and its distribution between the different soil fractions.

Keywords: Mine tailings, contaminated soil, microcosms, bioaugmentation.

INTRODUCTION

The dumping of mine tailings containing heavy metals on natural soils has become a serious contamination issue in the mining district of Cartagena-La Unión, Spain (Robles-Arenas et al., 2006). Similar scenarios in different locations of the planet are causing a detrimental effect on the environment. Unlike many organic compounds that become innocuous overtime, heavy metals are persistent in nature (Kelly et al., 1996). Nevertheless, soils activate decontamination mechanisms such as the action of certain microorganisms to mobilize metals from labile to less available soil fractions (Brady et al., 1999).

Soils differences related to geological, physiographic and climatic aspects have an effect on the indigenous microbiota and that could modify the decontamination mechanism. Heavy metals mobility in soils depends on both its distribution in soil fractions and the environmental conditions prevailing in the natural ecosystem (pH, redox potential (ORP), salinity, microbial consortia, temperature, etc.).

A microcosm can be considered a model at laboratory scale of a natural system that provides, in a short time, information on the biochemical processes involved. Bioaugmentation is, besides biostimulation, one of the existing possibilities to modify the soil decontamination process by increasing the indigenous microbial population of the ecosystem with the external addition of metabolically active microorganisms. In the present study, that bioprocess was investigated and the physicochemical changes provoked were monitored both in the aqueous phase (pH, ORP, metals in solution) and in the solid phase (metal distribution in different fractions).

EXPERIMENTAL

Contaminated soil

The contaminated soil (CS) was sampled in an area nearby Llano del Beal (Sierra Cartagena-La Unión, Murcia). In microcosm tests, the soil particle size was conditioned to <1 mm (Gommy, 1997). Chemical analyses were performed in triplicate by acid digestion followed by determination of metal contaminants by atomic absorption spectrometry: 25.01% Fe, 0.52% Zn and 0.80% Pb. The mineralogical characterization by X-ray diffraction revealed the presence of pyrite in a matrix of quartz with Al and Fe silicates. In addition, a sequential extraction (SE) chemical analysis, performed in triplicate and considering six soil fractions (exchangeable, organic, carbonates, hydroxides, sulfides and residual), confirmed that the main soil contaminants were metal sulfides.

Microbial culture

The microorganisms used in the bioaugmentation process were obtained from the own soil. The S-oxidizing ability of the strain was achieved by contact between the soil (10 g), 0K nutrient medium (90 mL) and elemental sulphur (1 g). Before inoculation, the strain was grown for 20 days in three consecutive transfers. In spite of that, the microbial culture did not necessarily lose its Fe-oxidizing ability.

Microcosms

The microcosm tests were performed in Erlenmeyer flasks, containing 10 g of CS and 90 mL of 0K medium, in an orbital shaker at 150 rpm and 35°C. The contaminated soil was tested both in sterilized (microcosms Control and S-ox) and non-sterilized conditions (microcosms Native and Mixture), supplementing microcosms S-ox and Mixture with the addition of 10 mL of the microbial strain of S-oxidizing microorganisms. Periodically, pH, ORP and metal concentration (Fe and Zn) were measured in solution. After 49 days, the solid residues were dried and analyzed following a sequential extraction procedure similar as for the as-received CS.

RESULTS AND DISCUSSION

pH and redox potential measurements

pH and ORP are physicochemical parameters that can be used to predict microbial activity.

The evolution of both parameters, depicted in Figure 1, indicates that the beginning of bacterial activity in the microcosms establishes differences from day 7th on. In fact, the higher acidity associated to more oxidizing conditions was recorded in the bioaugmented microcosms (S-ox and Mixture) followed by the microcosm using indigenous microorganisms (Native). Thus, in the microcosms with microbial activity, values of pH and ORP close to 1 and 680 mV, respectively, were reached. In contrast, the values obtained in the microcosm Control were 2.4 and 340 mV, respectively. This behaviour is related to a greater production of H_2SO_4 during the chemical oxidation of mineral sulfides mediated by S-oxidizing and Fe-oxidizing microorganisms, according to reactions 1, 2, 3 and 4 (Ballester et al, 2000; Jennings et al, 2000). It is expected that both types of microorganisms would be present in the microcosms, in higher or less degree, whether by inoculation or supplied by the own soil.

$$MeS + Fe_2(SO_4)_3 \longrightarrow MeSO_4 + FeSO_4 + S^\circ \quad (1)$$

$$S^0 + H_2O + 3/2\, O_2 \xrightarrow{S-oxidizers} H_2SO_4 \quad (2)$$

$$FeS_2 + 7/2\, O_2 + H_2O \longrightarrow FeSO_4 + H_2SO_4 \quad (3)$$

$$2Fe^{2+} + 1/2\, O_2 + 2H^+ \xrightarrow{Fe-oxidizers} 2Fe^{3+} + H_2O \quad (4)$$

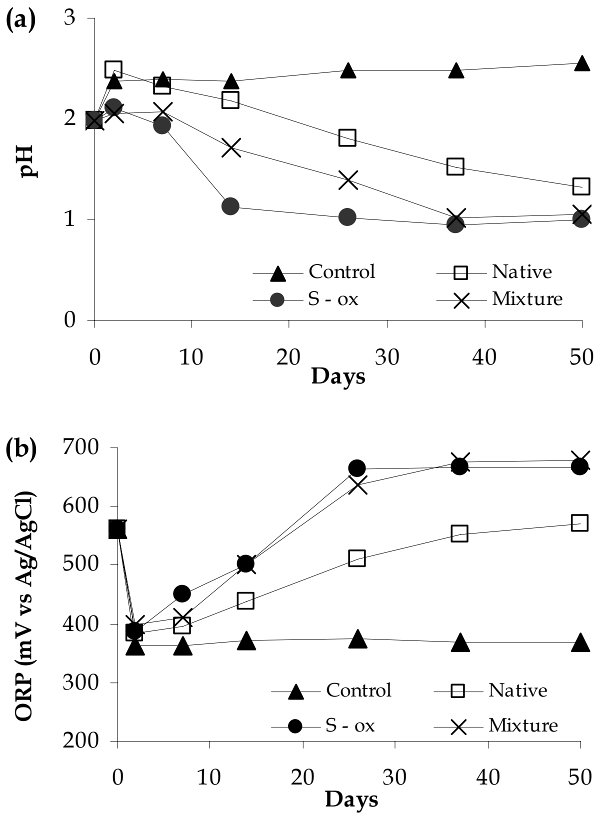

Figure 1. Evolution of pH (1a) and ORP (1b) vs time.

Metals dissolution

The aggressive conditions generated by microbial activity would promote the dissolution of metals from the soil.

As shown in figure 2a, the iron concentration in solution increased gradually in the three microcosms with microbiological activity. However, the higher iron dissolution was recorded in the microcosms inoculated with S-oxidizing microorganisms, high above the values recorded in microcosms without bioaugmentation (Native and Control). The fact that it is microcosm S-ox, instead of microcosm Mixture, the first to show up an increase of iron on day 7th, associated to a decrease of pH and to an increase of ORP (figure 1), seems to indicate a better adaptation of the S-oxidizing strain to the sterilized than to the non-sterilized soil and that microorganisms present in the soil delayed the oxidation of Fe in favour of the S-oxidizing strain.

Unlike iron, the dissolution of zinc started uniformly and instantly in all microcosms (figure 2b). The more marked differences were recorded after day 7th, when microcosm Control reached stationary conditions while Zn concentration increased in the rest of microcosms. That would be an indication of a dissolution process in two stages: in the first stage, zinc is easily leached from the soil while oxidizing conditions, generated by microbial activity, are required in the second stage.

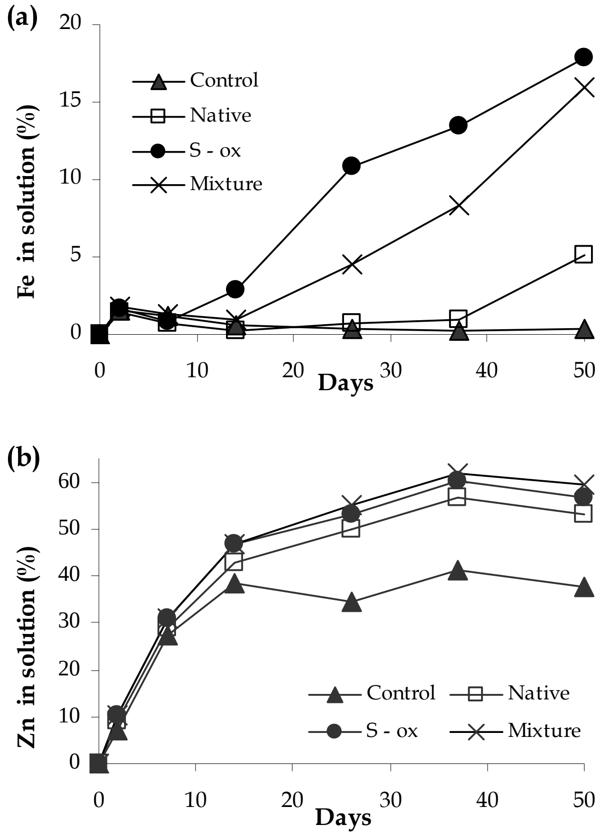

Figure 2. Metals dissolved in the microcosms: a) iron and b) zinc.

Metal distribution in solid residues

The biochemical reactions that took place in the microcosms affected the composition of both the aqueous and the solid phases. After 49 days, solid residues were analyzed following a sequential extraction procedure, a slight variant of the EPA procedure (Brady et al., 1999), to determine the new distribution of metal contaminants (Fe, Zn and Pb) in the different soil fractions.

In the case of iron (figure 3a), its mobilization from the sulfides to the residual soil fraction and to the leached phase is quite evident because of the low iron concentration in the more labile soil fractions (exchangeable, organic, carbonates and hydroxides). Considering the values of the as-received CS, the marked difference observed between the biotic microcosms, especially the microcosm S-ox, and the abiotic microcosm, Control, would be attributable to the action of microorganisms (both inoculated and indigenous) present in the contaminated soil. That is in agreement with the amounts of iron in solution observed: the higher the microbial activity is the higher the mobilization of iron and the more pronounced its decrease in the sulfides soil fraction.

On the other hand, zinc was easily mobilized from the more labile soil fractions to the aqueous phase (figure 3b). This is an indication that the zinc weakly adsorbed can be dissolved from those soil fractions in mild environmental conditions of pH and ORP (Li et al, 2001; Gleyzes et al, 2002). That would be in agreement with the dissolution of Zn observed during the first stage in all microcosms (figure 2b). Since more oxidizing conditions are required in order to release zinc from the sulfides soil fraction such effect is only detectable in the microcosms with microbiological activity, in agreement with the dissolution of Zn observed during the second stage (figure 2b). Then, the absence of microbial activity in the microcosm Control would clearly condition the dissolution of Zn from the less labile soil fractions.

Unlike Fe and Zn, lead did not migrate towards the leached phase because of its precipitation in the leaching medium as insoluble sulfate. Mobilization of Pb from more labile soil fractions occurred in all microcosms, but mobilization was not so clear from the sulfides fraction. In that case, the results seem to indicate that the mobility of Pb towards the residual soil fraction was higher in the microcosm without microbial activity (Control). The working hypothesis is that, for the rest of microcosms, the microbial activity and the presence of monovalent cations (Na^+ and K^+) supplied by the 0K nutrient medium, promoted the formation of plumbojarosite ($PbFe_6(OH)_{12}(SO_4)_4$). According to the literature, that basic sufate salt should be solubilized by the chemical reagent used to dissolve the sulfides soil fraction. (Deveci, 2004). In addition, the observation of a higher content of Pb in the residual soil fraction for the microcosm Control remains unclear and need further investigation.

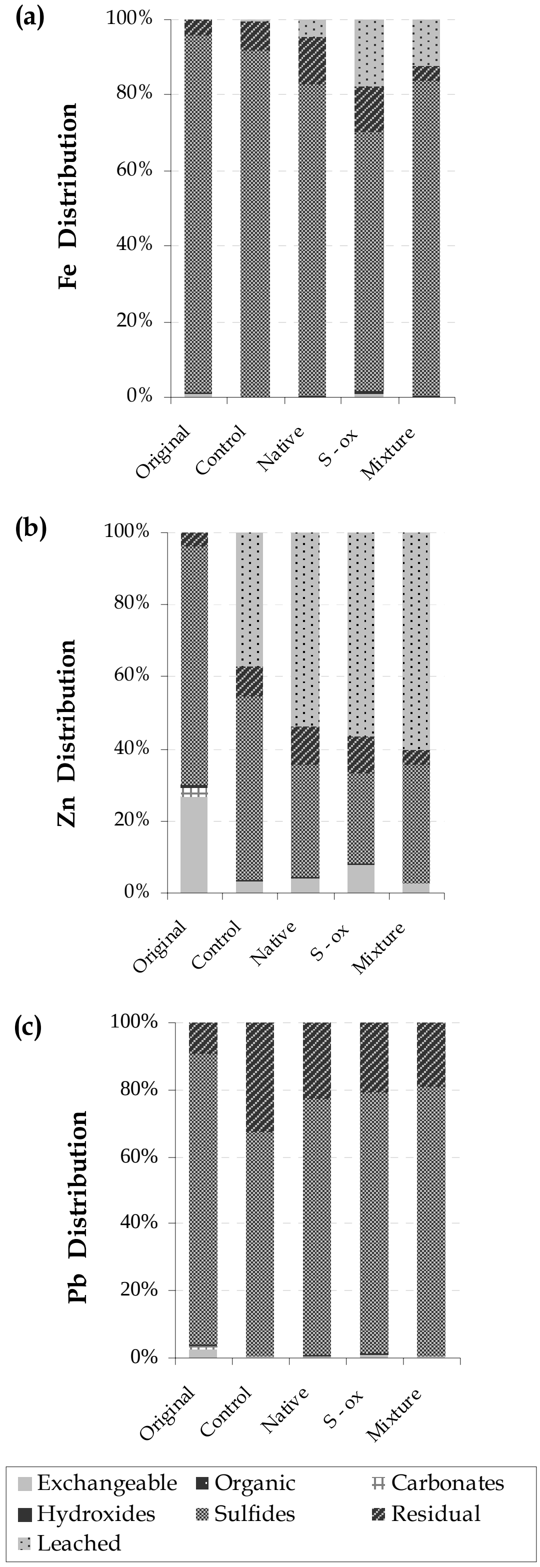

Figure 3. Distribution of metals in the different soil fractions for the residues collected in the microcosms: a) iron, b) zinc and c) lead.

CONCLUSIONS

The microcosm tests performed with a soil contaminated with metal sulfides showed that bioaugmentation with S-oxidizing microorganisms led to a higher mobilization of Fe and Zn towards the aqueous phase than in the different soil fractions. Conversely, Pb was mobilized, both in biotic and abiotic microcosms, towards less available soil fractions

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